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PRODUCED BY X-RAYS USING THE

NICKEL-HYPOPHOSPHITE SYSTEM 3: THE

LATENT IMAGE AND TRAPPED HYDROGEN (NASA)

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DEVELOPABLE IMAGES PRODUCED BY X-RAYS USING THE NICKEL-HYPOPHOSPHITE SYSTEM

III - The Latent Image and Trapped Hydrogen

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16. Abstract <p>The hydrogen trapped in X-irradiated hypophosphites, phosphites, formates, oxalates, a phosphate, and some organic compounds was vacuum extracted and measured quantitatively with a mass spectrometer. After extraction, normally developable salts were found to be still developable. Thus, the latent image is not the trapped hydrogen but a species of the type HPO_2^-. The amplification factor for irradiated hypophosphites is about 100. A narrow range of wavelengths (at about 0.07 nm, 0.7 Å) is responsible for the formation of the latent image.</p>			
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SUMMARY

The hydrogen trapped in 16 X-irradiated compounds was vacuum extracted and measured quantitatively with a mass spectrometer. The compounds included five hypophosphites, two phosphites, two formates, two oxalates, one phosphate, and four organic compounds.

The data indicate that the latent image species of X-ray sensitive salts is an ion radical, that is, $\dot{\text{HPO}}_2^-$, $\dot{\text{PO}}_3^-$, or $\dot{\text{CO}}_2^-$. It is not the hydrogen found trapped in the salts. However, the amount of trapped hydrogen can in general be used as a measure of the latent image species being produced by the same reaction. By making use of this information, a narrow range of X-ray wavelengths (at about 0.7 nm, 0.7 Å) was found to be responsible for producing the latent image in nickel hypophosphite. Moreover, the amplification factor for hypophosphites was found to be about 100. This low amplification factor is attributed to the relatively high solubility of the irradiated salts.

INTRODUCTION

Research at Lewis Research Center has led to the discovery of a photographic-type process based on nickel (refs. 1 and 2). It resembles the common silver photographic process in that a latent image formed by radiation can be amplified by development to produce a visible image of wide tonal gradation in the gray scale. See figure 1. Our photographic emulsions contain nickel hypophosphite and although they are not sensitive to visible light, they are sensitive to X-rays and electron irradiation. This lack of sensitivity to visible light can be a distinct advantage in radiography and diffraction in that special lightproof cassettes and darkrooms are not necessary. A second advantage

is that relatively more abundant and less expensive nickel replaces the more costly silver in the conventional photographic emulsions. The nickel hypophosphite emulsion in its present state of art, however, is not as sensitive as the conventional photographic materials to X-rays. The exposure time for a good image is about 5 minutes at about 20 000 roentgens per minute with a tungsten target tube at 250 kilovolts.

Further work (ref. 3) indicates that at least five salts in addition to nickel hypophosphite are potentially usable in emulsions for our X-ray sensitive and developable process. These are sodium hypophosphite, lithium hypophosphite, ammonium hypophosphite, sodium phosphite, and nickel formate. The anions of such salts have been shown by electron paramagnetic resonance (EPR) studies to exhibit the following γ -irradiation-induced reactions:

For hypophosphites (refs. 4 and 5)



For phosphite (ref. 6)



For formate (ref. 7)

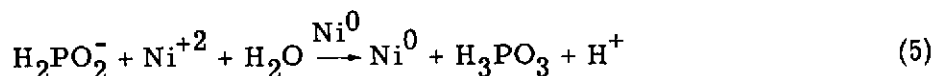


In all these reactions, atomic hydrogen ($\text{H}\cdot$) is produced from a hydrogen covalently bonded to the anion. This led us to postulate initially (ref. 3) that the hydrogen is trapped in the crystal lattice and that it is this trapped reducing species, $\text{H}\cdot$ (trapped), which accounts for the latent image of our photographic process.

We have also tentatively postulated (refs. 3 and 8) that during development this trapped hydrogen species reduces the nickel ion Ni^{+2} in the developer to nickel metal, Ni^0 , with the formation of hydrogen ions H^+ .



The minute amounts of nickel thus formed autocatalyze the well-known reaction characteristic of electroless plating (refs. 9 and 10).



This autocatalytic reaction accounts for the amplification of the image.

The purpose of this investigation was to test some of the postulates of our proposed mechanism and to modify them as required. In particular, we wanted to know if hydrogen is trapped in irradiated sensitive salts and if such hydrogen can account for the latent image. The investigation involved the mass spectrometric measurement of the amount of hydrogen trapped in various irradiated compounds, including several developable salts (e.g., nickel hypophosphite). Also studied were the effect of hydrogen removal on the development of irradiated compounds, the retention of hydrogen at atmospheric pressure, and the dependence of the amount of hydrogen on sample size.

APPARATUS, PROCEDURE, AND RESULTS

Table I lists the compounds investigated. The hydrogen formed in the compounds by X-irradiation was determined as follows: A known quantity of the compound (less than a gram) was placed in an aluminum boat (inside dimensions, 5 cm by 0.6 cm by 0.6 cm; wall thickness, 0.1 cm). The use of a platinum or gold boat instead of an aluminum boat did not alter the results. The sample was exposed for about 1 hour to 250-kilovolt, 10-milliampere X-rays from a tungsten target tube with the sample 10 centimeters from the target. The dose rate was 660 000 roentgens per hour under these conditions. The actual exposure time (which determined the dose) and the actual weight of the sample were selected to produce easily measurable rates for hydrogen gas evolution.

Within 5 minutes after irradiation the measurement of the hydrogen gas evolved at room temperature ($23 \pm 1^\circ \text{C}$) was begun. For this measurement we adapted a system developed recently at the Lewis Research Center (ref. 11) for the determination of hydrogen in titanium metal. The aluminum boat and its contents (either irradiated or un-irradiated sample) were placed in a 10-centimeter-long glass tube with a 19/38 standard taper joint at the top. This tube was connected to the manifold of the apparatus as depicted in figure 2 and evacuated by the auxiliary pump for 15 seconds. (This discarded gas proved to contain a negligible percent of the hydrogen trapped in the sample.) Immediately after this, the evolved gas was pumped by means of the three-stage mercury diffusion pump into the mass spectrometer's expansion volume, where the gas could be analyzed quantitatively. A liquid nitrogen trap between the pump and the sample prevented condensable vapors such as water from entering the expansion volume. Under the room-temperature conditions used, evolution was relatively slow and required 10 hours for the removal of about 95 percent of the hydrogen and 24 hours for 98 percent removal.

Elevated temperature was avoided because of possible decomposition of some of the compounds (e.g., the hypophosphites). The gas collected was essentially pure hydrogen. No hydrogen was found in unirradiated samples.

The mass spectrometer used, a Consolidated Electrodynamic Corporation Model 21-614, was sensitive to nanogram quantities of hydrogen. Its calibration is described in reference 11. The data listed in table I are in general the average of several determinations. They are corrected for the mass spectrometer background (about 4 ng/run) and the collection system blank (about 24 ng/hr).

After removal of essentially all the hydrogen, development of some of the salts (table I, column 4) was attempted. The results in column 5 show that removal of the hydrogen had no effect on the development. The development procedure (variation of the method described in refs. 3 and 8) consisted of adding 1 cubic centimeter of the developer to the salt and letting the sample with developer sit 24 hours. The developer consisted of 3 normal ammonium hydroxide containing 4 percent sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 4 percent nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), and 4 percent ammonium chloride (NH_4Cl). In the case of irradiated $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, the nickel formed during development was determined gravimetrically by washing, drying, and weighing. These results are given in table II and illustrate even more clearly that the trapped hydrogen does not have to be present for development to take place. The weight of nickel is the same irrespective of the presence of trapped hydrogen.

To determine how well the hydrogen is trapped in irradiated $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$, irradiated samples were allowed to stand various times (3 to 15 days) in air before the amount of trapped hydrogen was determined. The results given in table III indicate that indeed in air at atmospheric pressure, the hydrogen formed during irradiation is trapped in the solid. There is no decrease of hydrogen with standing time.

The dependence of the hydrogen concentration upon sample weight was also determined. In figure 3, the hydrogen concentration per dose C/D is plotted as a function of sample weight. There is a definite decrease of C/D with increasing weight.

DISCUSSION OF RESULTS

Nature of Latent Image

From table II, we see that X-irradiated $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ is developable even though over 99 percent of the initially trapped hydrogen is removed by vacuum extraction. Moreover, it appears that the actual weight of nickel metal formed by development does not depend on the presence of the trapped hydrogen. Similar results were found for $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_2$, and $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ (table I). Thus, we conclude that the

trapped hydrogen is not the latent image species. Additional evidence is the fact that irradiated compounds such as K_2HPO_4 and $NiC_2O_4 \cdot 2H_2O$ contain trapped hydrogen (table I) but nevertheless are not developable (ref. 3).

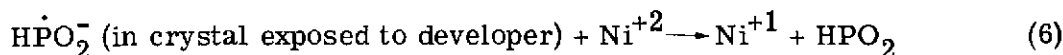
Referring to equations (1) to (3)

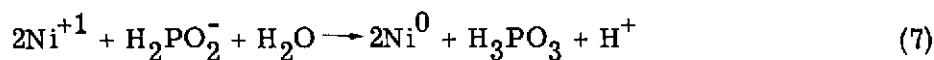


we are led to believe that the ion radicals $\dot{H}PO_2^-$, $\dot{P}O_3^{2-}$, and $\dot{C}O_2^-$ comprise the latent image species in their respective salts. However, several problems arise that require some discussion. These problems for the most part involve the question, "Why are some salts not developable even though the proper ion radical, the latent image species, is produced by radiation?" Among this group of salts are some hypophosphites (e.g., $Ca(H_2PO_2)_2$), a formate ($NaCHO_2$), and the oxalates (e.g., $Na_2C_2O_4$).

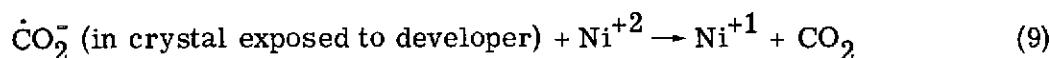
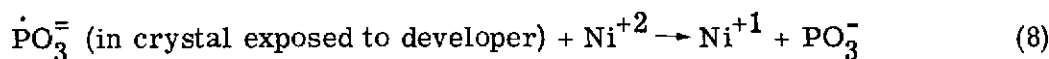
The most obvious answer might involve the relative concentration of the latent image species. Because the latent image species is produced simultaneously with the hydrogen atoms (eqs. (1) to (3)), the concentration of hydrogen can be used as a measure of the concentration of the latent image species (see the following section). Table I gives values of C/D (hydrogen concentration per roentgen) for the various salts. The value of C/D for $NH_4H_2PO_2$ is smaller than C/D for $Co(H_2PO_2)_2$ and comparable with C/D for $Ca(H_2PO_2)_2$. Yet irradiated $NH_4H_2PO_2$ is found to be developable, while the other two hypophosphites are not. Furthermore, for both $NaHCO_2$ and $Ni(HCO_2)_2 \cdot 2H_2O$, the values of C/D are about equal. Nevertheless, the latter is developable and the former is not. Our evidence, however, does not preclude entirely the effect of the latent image species concentration on the ability to develop an irradiated salt. Obviously, for any specific salt, the ability to develop the latent image should be proportional to the concentration of the latent image species to the first approximation.

From our experience, we believe a far better explanation and answer to our question involves the development process. The initial development reactions involve the formation of small quantities of catalytic nickel. For an irradiated hypophosphite the reactions can be represented as follows:

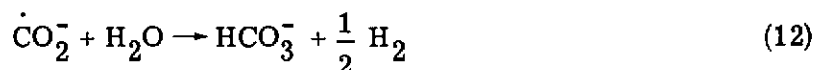
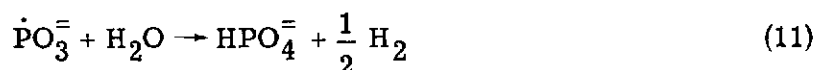
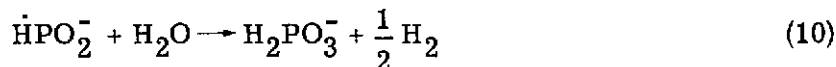




In the first reaction, the latent image species reduces divalent nickel in the developer (or salt) to monovalent nickel. In the second reaction the monovalent nickel is reduced by hypophosphite in the developer to catalytic metallic nickel. The second reaction is the same regardless of the irradiated salt used. The first reaction of course depends upon what latent image species is present. For phosphites and formates (ref. 12) the respective initial reactions would be



If these were the only reactions with which to be concerned, we would expect all irradiated hypophosphites, phosphites, formates, and oxalates (ref. 13) to be developable. However, competing reactions exist during the initial development step which involve destruction of the latent image species without the production of catalytic nickel metal (ref. 8). They may be depicted as follows:



In these reactions, hydrogen gas is produced instead of nickel metal.

Experimentally (ref. 8), it has been shown that rapid enough agitation during the development of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ prevents the precipitation of metallic nickel. Thus, rapid dissolution must favor reaction (10) over reaction (6). Moreover, the greatest sensitivity was attained when development involved simply exposing the irradiated nickel hypophosphite emulsion to moist ammonia vapor (unpublished data from Lewis). By this treatment the dissolution of the salt is minimized. Of course, development in moist ammonia may be used only for developable nickel salts. However, these data support the premise that minimizing the dissolution rate should increase the sensitivity of all

developable salts. We believe that the difference in sensitivity between apparently similar salts may be accountable to differences in their solubilities or rates of dissolution.

Moreover, other properties of a crystal could certainly be expected to have some bearing on the development of a particular salt. For example, the presence of the nickel ion in the irradiated crystal should favor development over destruction of the latent image. Experimentally (unpublished data from Lewis), only two salts have been found to be developable when in the form of gelatin emulsions. They are $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{CHO}_2)_2 \cdot x\text{NH}_3$. Both contain the nickel ion.

The irradiated organic compounds shown in table I are not developable and contain little or no trapped hydrogen. It is therefore assumed that any organic radicals produced by radiation do not persist in the solid for a significant length of time after irradiation.

Several compounds deserve special comment. We have thus far been unable to develop irradiated $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ although it contains both CO_2^- and the nickel ion, as well as trapped hydrogen. We have, at present, no specific explanation for this. Because cobalt can also be electroless plated, we would at first expect that $\text{Co}(\text{H}_2\text{PO}_2)_2$ would be as sensitive to X-irradiation and subsequent development as the corresponding nickel salt. However, recent work (ref. 14) indicates that the presence of ammonia in our developer does not allow the desired autocatalytic reaction for cobalt to occur.

Trapped Hydrogen as Measure of Latent Image Species

For the anions H_2PO_2^- , $\text{HPO}_3^{=}$, and HCO_2^- , equations (1) to (3) show that for every hydrogen atom produced, a latent image species is formed. In addition, this hydrogen remains trapped: for $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ in air, at least 15 days (table III). Thus, the hydrogen concentration can be used as a measure of the latent image species concentration, and C/D can be used as a measure of the number of latent image species per dose.

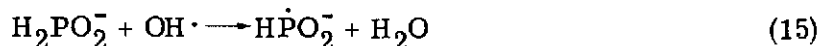
Measurement of the hydrogen may have certain advantages over the direct measurement of the latent image species by EPR. First, the compounds of most interest are $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{CHO}_2)_2 \cdot x\text{NH}_3$. Both contain divalent nickel, which will mask the desired EPR signal. In contrast, nickel does not hinder the determination of trapped hydrogen by our method. Second, in practice it may be desirable to study the irradiation of the salts present in films or emulsions. This is easier to handle in our experimental setup than by EPR. Third, samples should be thin to prevent self-shielding (discussed in the section Effective X-Ray Wavelength). However, single crystals should be

used for the best EPR measurements of the number of spins. Of course, there are some situations where direct measurement of the latent image species is the only satisfactory means.

In most cases, the trapped hydrogen can be used as a gross measure of the latent image. However, to use the trapped hydrogen as a precise measure, care must be taken because of possible interferences. For instance, trapped hydrogen may be produced by an auxiliary independent reaction during irradiation. For example, consider the irradiation of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. For this compound the trapped hydrogen and the latent image species could be produced by two different and perhaps independent reactions:

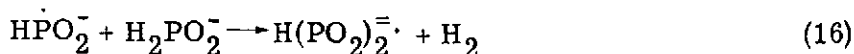


If this be the case, the number of trapped hydrogen atoms would not in general equal the number of latent image species, but the two numbers would be proportional because both should be proportional to the dose. During the irradiation of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, some of the trapped hydrogen is likely produced by reaction (13) in that C/D is larger for the hydrate than for the anhydrous salt (table I). However, because no $\text{OH}\cdot$ signal is found by EPR, we believe a rearrangement of the following type to occur:



Thus, there would be again a one-to-one correspondence between the number of trapped hydrogen atoms and the number of latent image species. Rearrangements may, of course, occur for all the irradiated hydrated salts. Thus, the possibility exists that water of hydration may be effective in increasing (i.e., doubling, tripling, etc.) the concentration of the latent image.

Another interference that complicates the use of the trapped hydrogen as a measure of the latent image may arise from secondary reactions that are reported to occur even after irradiation (ref. 4):



This hydrogen may also be trapped insofar as the data in table III imply that C/D of irradiated $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ may increase with time. According to reaction (16), the

species HPO_2^- should decrease with time, while the trapped hydrogen might increase. However, if we speculate that $\text{H}(\text{PO}_2)_2^-$ may also serve as a latent image species, the effective number of latent image species would not change. Regardless, because of the occurrence of reaction (16), C/D should be determined immediately after irradiation to be a meaningful measure of the latent image species produced.

Amplification Factor

One of the obvious uses of the hydrogen concentration as a measure of the latent image species is in the computation of the amplification factor. In a previous report (ref. 8), the yield of nickel metal was studied as a function of various parameters for $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$. A yield Y was about $5.6 \times 10^{-7} \text{ g}_{\text{Ni}}(\text{g}_{\text{samp}})^{-1} \text{R}^{-1}$ (fig. 2 of ref. 8: 0.21 g/g for $3.75 \times 10^5 \text{ R}$). In table I, we now report for $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, a C/D of $38 \times 10^{-12} \text{ g}_{\text{H}_2}(\text{g}_{\text{samp}})^{-1} \text{R}^{-1}$. The amplification factor θ is

$$\theta = \frac{Y/(\text{Equivalent weight of nickel})}{\left(\frac{C}{D}\right)/(\text{Equivalent weight of hydrogen})} = \frac{5.6 \times 10^{-7}/58.7}{38 \times 10^{-12}/1} \approx 250 \quad (17)$$

The equivalent weights are based on equations (1) and (9). Similarly, the amplification factor for $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ can be calculated from data in tables I and II:

$$\theta = \frac{0.0052/0.0441/1.34 \times 10^6/58.7}{54 \times 10^{-12}} \approx 30 \quad (18)$$

The amplification factors calculated here should not be taken as more than order-of-magnitude values because of the probably large dependence on the specific development conditions used. We would expect that under nearly identical development conditions, the amplification factor for $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ would be greater than that for $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

Of more importance is the fact that the amplification factors are quite small as compared with that for the silver halide process, which is over a million. This small amplification is undoubtedly the major reason for the insensitivity of our process (as mentioned in the INTRODUCTION). Thus, any attempt to improve the sensitivity of the system should be directed to the development step. As discussed previously there are competing reactions during the initial development step. It may be that the majority of the latent image species dissolve without development. Only a fraction of the latent

image may actually be developed. The fraction which develops may have a very high amplification factor, but the observed (experimental) amplification factor would be the product of this high value and the very small fraction of latent image which actually develops. A decrease in the dissolution rate of the irradiated salt during development ought to increase the observed amplification factor.

Effective X-Ray Wavelength

The decrease of C/D with sample weight in figure 3 is understandable in terms of self-shielding of the sample from X-rays. Parts of a sample at a distance x below the surface see a lower dose D_x than does the surface. The value of D_x depends on the mass absorption coefficient μ_m and the density ρ as follows:

$$D_x = D \exp(-\mu_m \rho x) \quad (19)$$

The average dose for the sample \bar{D} is then

$$\bar{D} = \frac{D \int_0^{x^*} \exp(-\mu_m \rho x) dx}{x^*} = D \left[\frac{1 - \exp(-\mu_m \rho x^*)}{\mu_m \rho x^*} \right] = D \left[\frac{1 - \exp(-\mu_m w/b)}{\mu_m w/b} \right] \quad (20)$$

where x^* is the thickness of the sample, w the weight of sample, b the cross-sectional area (about 3 cm^2 for our experimental setup) and

$$x^* = \frac{w}{\rho b} \quad (21)$$

Multiplication of the final form of equation (20) by $C/(D \cdot \bar{D})$ yields

$$\frac{C}{D} = \frac{C}{\bar{D}} \left[\frac{1 - \exp(-\mu_m w/b)}{\mu_m w/b} \right] \quad (22)$$

where C / \bar{D} is a constant.

Using equation (22) we curve fit the data in figure 3. The solid line shown in this figure corresponds to a μ_m of $10.5 \text{ cm}^2/\text{g}$. For $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$ such a value for μ_m corresponds to a wavelength λ of about 0.07 nanometer (0.7 Å). The calculations

were made by using handbook values for the required atomic absorption coefficients (ref. 15). The irradiation (250-kV X-rays) used had a Duane-Hunt limit λ_0 of 0.005 nanometer (0.05 Å) and a maximum intensity at 0.0075 nanometer (0.075 Å) (ref. 16). The μ_m for 0.0075 nanometer (0.075 Å) is about 0.164. This low value for μ_m could not account for the relatively large decrease in C/D observed in figure 3. We, therefore, interpret the data to mean that X-rays of approximately 0.07-nanometer (0.7 Å) wavelength ($\mu_m = 10.5 \text{ cm}^2/\text{g}$) are the most effective for inducing reaction (1) to occur for $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$. The reaction produces both trapped hydrogen and the latent image species. Some of the data in figure 3 indicate a steeper initial slope than does the calculated curve. If this be the case, μ_m would be higher, corresponding to a still longer wavelength.

The intensity I_λ of a narrow wavelength is linearly dependent on the voltage V (ref. 17):

$$I_\lambda = \frac{\epsilon}{\lambda^2} \left(\frac{1}{\lambda_0} - \frac{1}{\lambda} \right) = \frac{\epsilon}{\lambda^2} \left(\frac{V}{12400} - \frac{1}{\lambda} \right) \quad (23)$$

where ϵ is a constant. In contrast, the integrated intensity I_{cont} over all wavelengths depends on the square of the voltage (ref. 15).

$$I_{\text{cont}} = K'V^2 \quad (24)$$

where K' is a constant. Experimental evidence (fig. 3 of ref. 8) indicates a linear dependence of nickel yield on voltage in keeping with the concept that a narrow wavelength range is responsible for the latent as well as the visible image.

The values $\mu_m = 10.5 \text{ cm}^2/\text{g}$ and $\lambda = 0.07$ nanometers (0.7 Å) as calculated in this section are applicable only to $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$. The value of λ is likely to be different for phosphites and formates and may even vary a little for other hypophosphites because of crystal lattice interactions. Even if λ were the same, μ_m , of course, would depend on the actual composition of the salt.

Applicability of Findings to Other Systems

The irradiation of hypophosphites and other salts has applications other than in X-ray-type photography. In fact, it may be used in most cases where electroless nickel plating can be used, especially where it is desirable to nickel plate without heating. Our work at Lewis (ref. 2) suggests the use of this technique for the making of mirrors and

the fabrication of printed circuits. Note that the nickel metal thus produced is contaminated with 1 to 6 percent phosphorus as is the case for all electroless nickel plating.

CONCLUSIONS

The latent image in the nickel hypophosphite system is not trapped hydrogen but an ion radical such as $\dot{\text{H}}\text{PO}_2^-$, $\dot{\text{P}}\text{O}_3^{--}$, or $\dot{\text{C}}\text{O}_2^-$. Even though such species are produced by irradiation of a particular salt, development might not occur because of the high rate of dissolution in the developer. The presence of nickel ion in the irradiated salt is a highly desirable feature.

Hydrogen formed during the irradiation is trapped. And with caution a measurement of it can be used as a measure of the latent image species produced. Interferences can arise from extraneous reactions occurring either during or after the irradiation.

The amplification factor for hypophosphites is about 100 under present development conditions. This accounts for the low sensitivity of the nickel-hypophosphite system. The cause is believed to be the rapid rate of dissolution of the irradiated salt in the developer.

A narrow range of X-ray wavelengths (at about 0.07 nm, or 0.7 \AA) is chiefly responsible for the formation of the latent image as well as the trapped hydrogen in $\text{Ni}(\text{H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O}$.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 4, 1973,
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TABLE I. - HYDROGEN TRAPPED IN VARIOUS X-IRRADIATED COMPOUNDS

[Dose rate, 0.66×10^6 R/hr; target material, tungsten; voltage, 250 kV; current, 10 mA.]

Compound	Formula	Hydrogen yield, ^a C/D, $g_{H_2}(g_{\text{samp}})^{-1}R^{-1}$	Developable before H ₂ removal ^b	Developable after H ₂ removal
Nickel hypophosphite ^c	Ni(H ₂ PO ₂) ₂ · 6H ₂ O	54×10^{-12}	Yes	Yes
Sodium hypophosphite	NaH ₂ PO ₂ · H ₂ O	38	Yes	Yes
Ammonium hypophosphite	NH ₄ H ₂ PO ₂	5	Yes	Yes
Cobalt hypophosphite	Co(H ₂ PO ₂) ₂	18	No	(d)
Calcium hypophosphite	Ca(H ₂ PO ₂) ₂	5	No	(d)
Hydrous disodium hydrogen phosphite	Na ₂ HPO ₃ · 5H ₂ O	3	Yes	Yes
Anhydrous disodium hydrogen phosphite	Na ₂ HPO ₃	.5	No	(d)
Nickel formate ^c	Ni(CHO ₂) ₂ · 2H ₂ O	.3	Yes	(d)
Sodium formate	NaCHO ₂	.3	No	(d)
Nickel oxalate	NiC ₂ O ₄ · 2H ₂ O	.2	↓	(d)
Sodium oxalate	Na ₂ C ₂ O ₄	(e)		No
Dipotassium hydrogen phosphate ^f	K ₂ HPO ₄	.35		↓
Benzene phosphorous acid	C ₆ H ₅ PO ₂ H ₂	(e)		
p-Nitrophenyl formate ^f	pNO ₂ C ₆ H ₄ OCHO	.04		
p-Hydroxy-benzaldehyde ^f	pHOC ₆ H ₄ CHO	(e)		
Iodoform	CHI ₃	(e)	↓	(d)

^aThese values are essentially equal to the yield of latent image species in moles $(g_{\text{samp}})^{-1}R^{-1}$.^bRef. 3 and unpublished data from Lewis.^cBoth Al and Pt boats used.^dNot determined.^eZero within accuracy of method, about $10^{-14} g_{H_2}(g_{\text{samp}})^{-1}R^{-1}$.^fBoth Al and Au boats used.

TABLE II. - EFFECT OF HYDROGEN REMOVAL ON DEVELOPMENT OF

X-IRRADIATED Ni(H₂PO₂)₂ · 6H₂O[Dose, 1.34×10^6 R; target material, tungsten; voltage, 250 kV; current, 10 mA.]

Sample weights, g	Treatment between irradiation and development	Nickel metal obtained by development, g
0.0441, 0.0340	None; hydrogen not removed	0.0052, 0.0055
0.0391, 0.0314	About 98 percent hydrogen removed by 24-hour vacuum extraction	0.0061, 0.0074
0.0309, 0.0312	None; hydrogen not removed	0.0055, 0.0031
0.0305, 0.0305	About 99.3 percent hydrogen removed by 72-hour vacuum extraction	0.0039, 0.0048

TABLE III. - EFFECT ON HYDROGEN CONTENT
OF STANDING IN AIR AFTER IRRADIATION

[Dose, 0.67×10^6 R; target material, tungsten;
voltage, 250 kV; current, 10 mA.]

Sample weight, g	Standing time in air between irradiation and hydrogen analysis, days	Hydrogen content, $\text{g}_{\text{H}_2} (\text{g}_{\text{samp}})^{-1} \text{R}^{-1}$
0.0140	0	53×10^{-12}
.0142	3	92
.0144	7	76
.0139	15	76

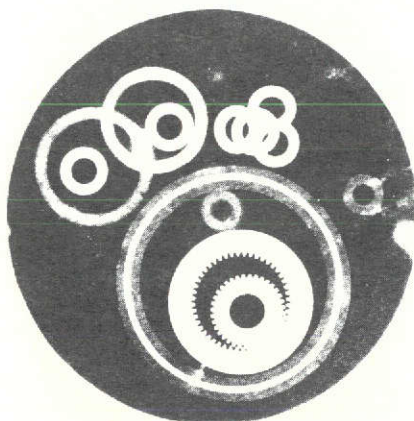


Figure 1. - Radiograph made using nickel
hypophosphite emulsion.

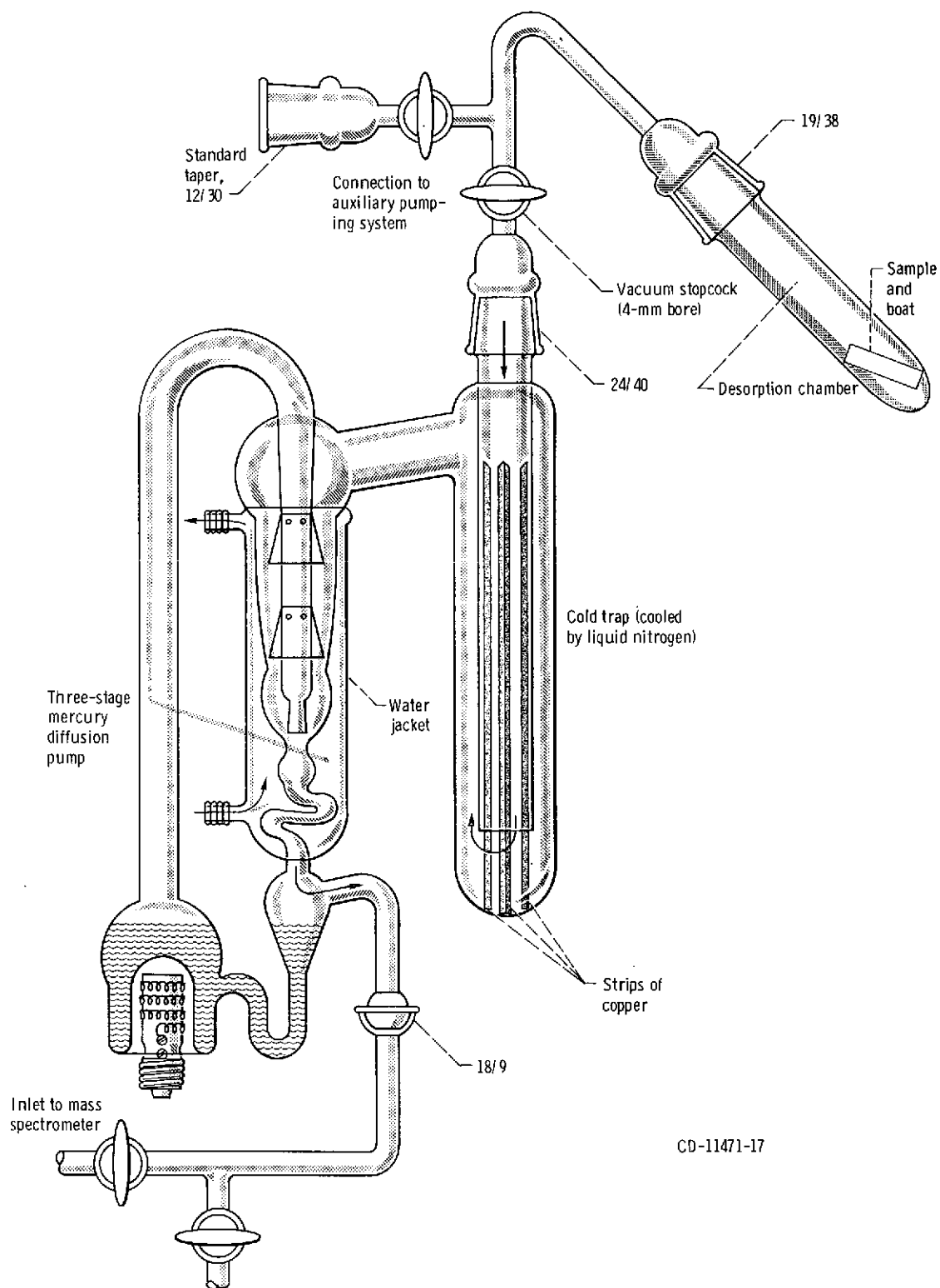


Figure 2. - Schematic drawing of desorption chamber and pumping system.

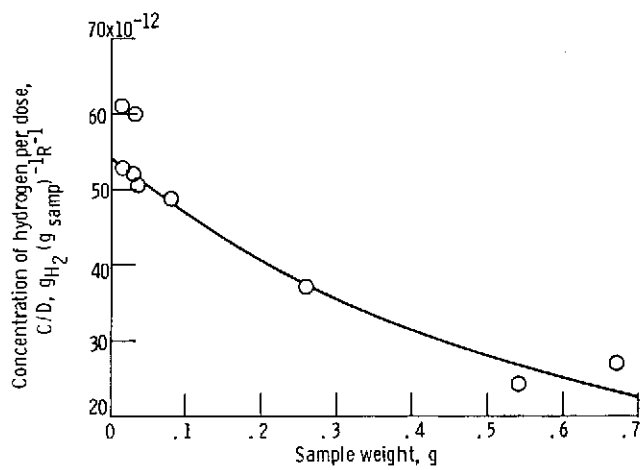


Figure 3. - Effect of weight of X-irradiated $Ni(H_2PO_2)_2 \cdot 6H_2O$ on hydrogen concentration. Dose rate, 0.66×10^6 roentgen per hour; target material, tungsten; voltage, 250 kilovolts; current, 10 milliamperes.